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FINAL REPORT

Theoretical and Experimental Studies of Molecular Dynamics

1 Oct 84 - 30 Sep 85

University of Chicago

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LPD

OCT 22 1985

October 16, 1985

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Major Larry Davis
Department of the Air Force
Air Force Office of Scientific Research
Bolling Air Force Base, D.C. 20332

Dear Major Davis:

As discussed in our last telephone conversation this letter contains my final ~~annual~~ report for Air Force Contract #49620 85C0003. (F49620-85-C-0003, Theoretical and Experimental Studies of Molecular Dynamics.

During the period of October 1, 1984 to September 30, 1985, the work described in the following papers was completed.

A Scattering Resonance Description of Very Low Energy Collision Induced Vibrational Relaxation. Stephen K. Gray and Stuart A. Rice, J. Chem. Phys. 83, 2818 (1985).

We report a study of very low energy collision induced vibrational relaxation using an approximate resonant state formalism which relates the inelastic cross section to the properties of metastable states. A study of models loosely based on the He + $I_2(B^3\Pi_{0_u^+})$ system reveals that the combined effect of a low collision energy resonance and high initial diatomic vibrational excitation can lead to a large enhancement of the vibrational relaxation cross section. In general, both the Wigner threshold requirement, $\sigma \propto k'^{-1}$, where k' is the initial relative momentum, and the existence of collision energy resonances can lead to increases in the very low energy relaxation cross section. Indeed, the threshold requirement increasingly enhances the contribution of a resonance to the cross section the closer the resonance is to zero collision energy. Because the density of resonances near zero collision energy is small, and because of the importance of the Wigner

threshold contribution, the collision dynamics near zero collision energy is very sensitive to the nature of the potential energy surface.

Time Dependent CARS as a Probe of Ground Electronic State Intramolecular Vibrational Redistribution. David J. Tannor, Stuart A. Rice and Peter M. Weber, J. Chem. Phys. (in press).

We describe a representation of coherent anti-Stokes Raman spectroscopy (CARS) suitable to the description of time dependent measurements. This representation includes the standard energy frame formulation as a special case when only CW fields are involved. The traditional CARS CW field frequency matching condition, $\omega_0=\omega_1-\omega_2+\omega_3$, must be generalized for non-CW fields; in that case it refers to the Fourier component at ω_0 of the convolution of the radiation field with the wavepacket recurrences. The influence of resonance, both in the ground and electronically excited states, on the decay of time delayed CARS signals is discussed. As expected, intramolecular vibrational redistribution on the ground state potential surface of a molecule causes the CARS signal to decay in time. Model calculations show that quantum beats in the CARS signal may be observed, reflecting either a small number of coupled states (strong and regular recurrences) or sequential coupling of states (weak and early recurrences).

Control of Selectivity of Chemical Reaction via Control of Wave Packet Evolution. David J. Tannor and Stuart A. Rice, J. Chem. Phys. (in press).

A time-dependent formulation of two-photon spectroscopy is employed to show that selectivity of reactivity can be achieved via coherent two photon processes. The problem of finding the optimum waveform (i.e. coherent pulse sequence) that will maximize the formation of a desired chemical species is formulated as a problem in the calculus of variations, and solved for two

different cases.

The Classical Mechanics of Vibrational Predissociation: A Model Based Study of Phase Space Structure and Its Influence on Fragmentation Rates. Stephen K. Gray, Stuart A. Rice and D.W. Noid, J. Chem. Phys. (submitted).

The classical dynamics pertinent to van der Waals molecule vibrational predissociation of a T-shaped model for $HeI_2(B)$ is examined. A fascinating phase space structure involving nonlinear resonances and stochastic motion is found. For low initial vibrational excitations of the I_2 partner of the vdW complex the relevant part of phase space is dominated by quasiperiodic motion indicating a purely quantal mode of decay ("dynamical tunneling"), but for higher initial vibrational excitations van der Waals molecule predissociation is a classically allowed process. Classically determined rates of decay agree to within a factor of three with the rates calculated from quantum mechanics.

Very truly yours,

Stuart A. Rice

Stuart A. Rice

Frank P. Hixon Distinguished Service

Professor of Chemistry

SAR:va